Solar Applications in Water Treatment

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Outline

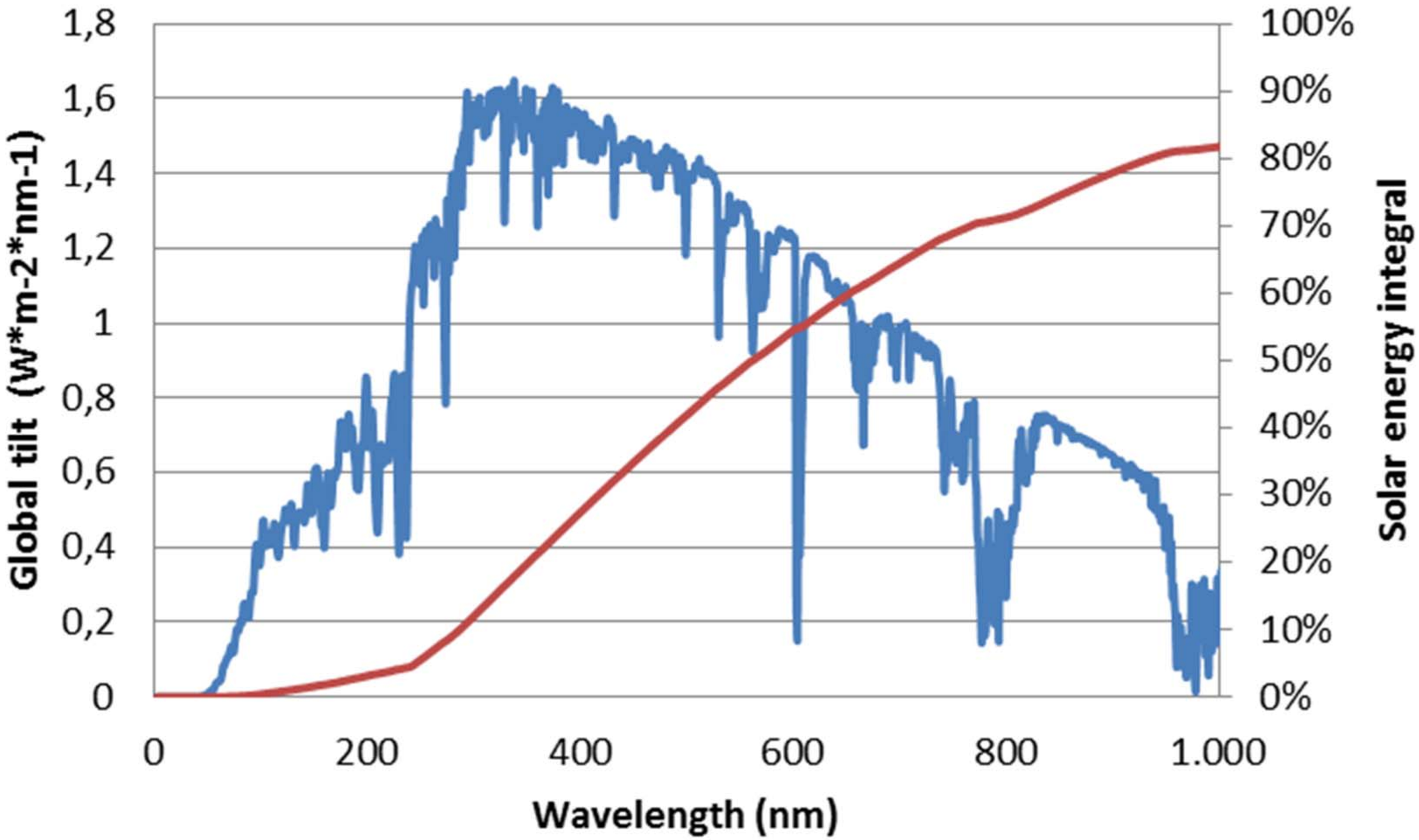
- Overview and history

- Example: SOWARLA - from laboratory to application
    - Sunlight utilization under Fenton conditions
    - Laboratory investigation for solar plant design
    - Process design for solar treatment plants
    - Solar treatment from prototype to demonstration scale

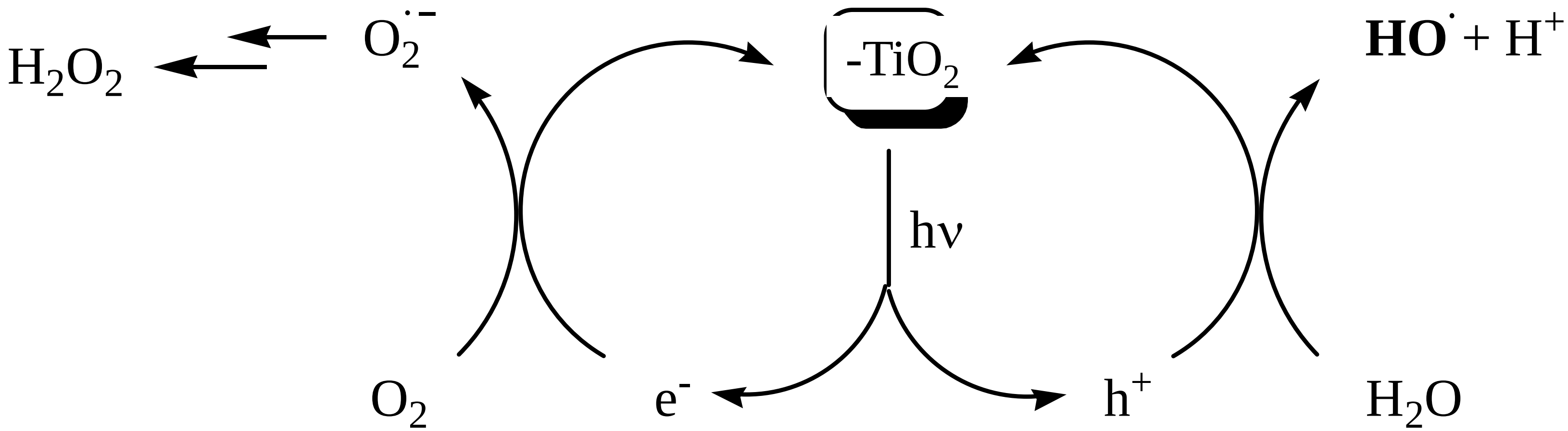
Solar Water Treatment - Overview

- The most researched solar chemical process
  - 10.000s of research papers
- Two main reaction classes that belong to the Advanced Oxidation Processes AOPs
  - Heterogeneous photocatalysis
    - Semiconductor photocatalysts – TiO_2
  - Homogeneous photocatalysis
    - Ionic photocatalysts – Fenton Reaction
- Mostly degradation of nearly all components known as contaminants
  - World wide activities
- Some work on the development of solar reactor systems up to commercial plants
  - Leaders are Spain and Germany

Solar Irradiation (ASTM G173-03)



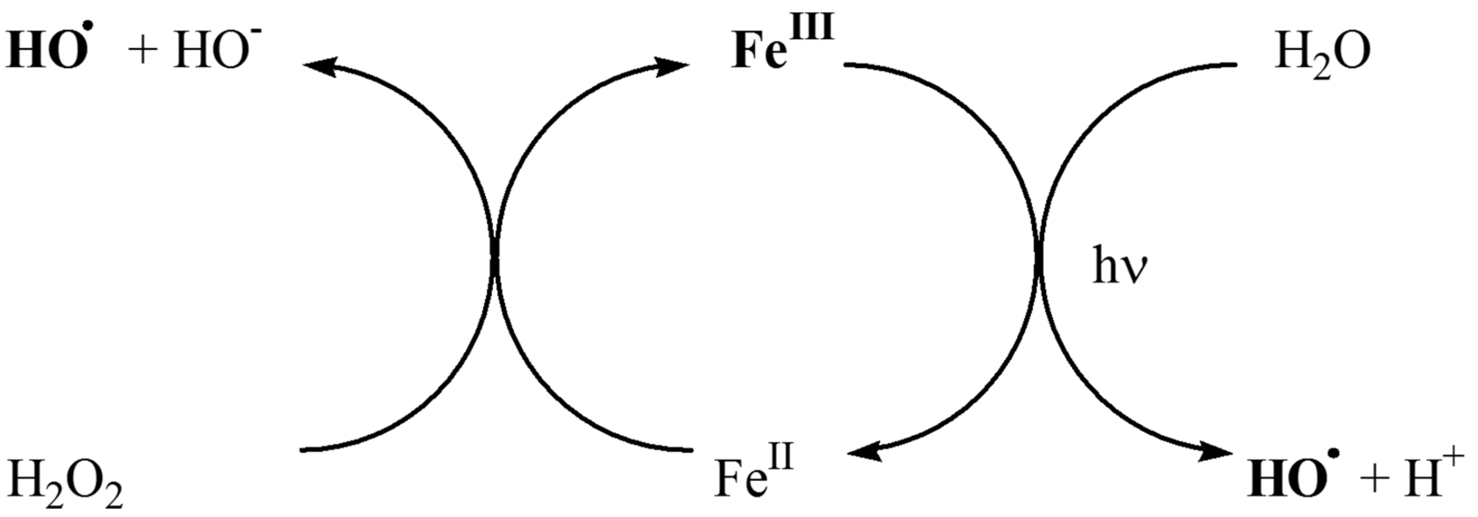
Semiconductor-Photocatalysis



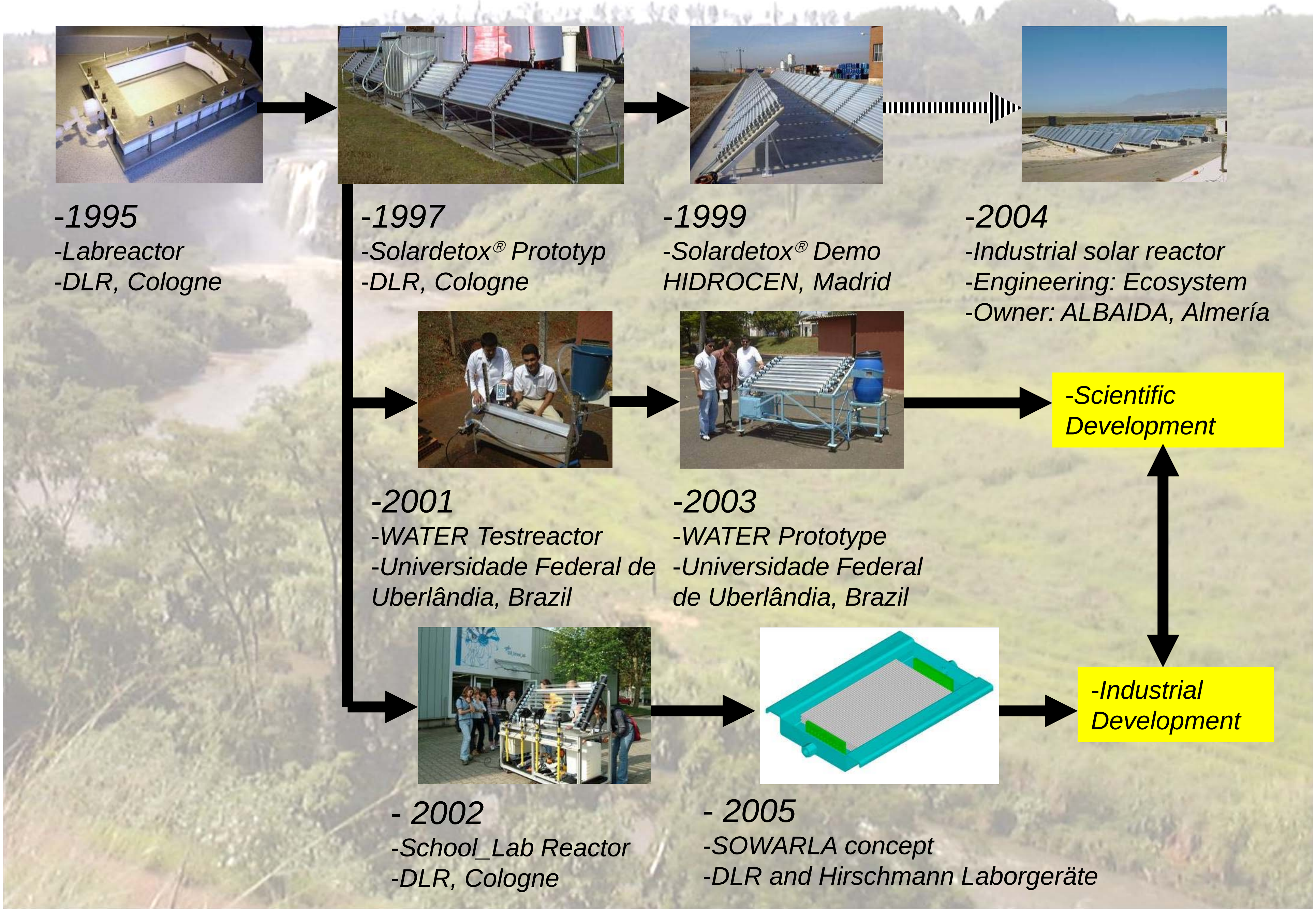
-UV-light of the solar spectrum (< 380nm) is absorbed by the semiconductor TiO_2, relatively stable electron/k elektron hole pairs are formed

-They react as well reducing as oxidising and by activating oxygen or H_2O_2 they can degrade nearly al organic substances and change the oxidation stages of inorganic ions

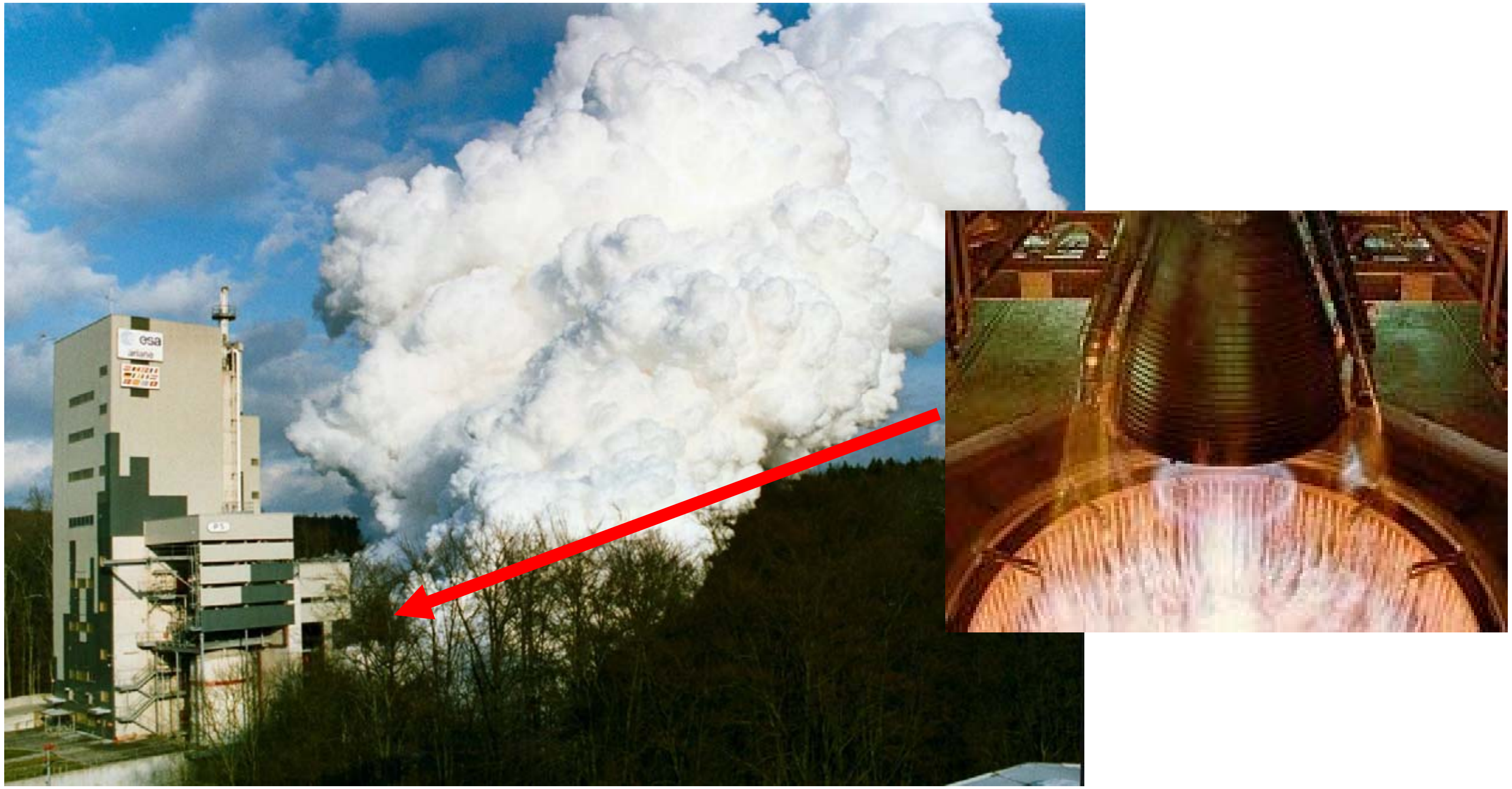
Light enhanced Fenton reaction



- pH fixed: 2.8 - 3.2
- Fe^{III} reduction in acidic solution proven up to 440 nm (λ_{max} LED)
- Photolysis of Fe^{III} complexes up to 580 nm
- Simple catalyst separation via precipitation and filtration
- Catalyst recycling by dissolving in acid for new batch/feed


-1995
-Labreactor
-DLR, Cologne
-1997
-Solardetox® Prototyp
-DLR, Cologne
-1999
-Solardetox® Demo
HIDROCEN, Madrid
-2004
-Industrial solar reactor
-Engineering: Ecosystem
-Owner: ALBAIDA, Almería
-2001
-WATER Testreactor
-Universidade Federal de
Uberlândia, Brazil
-2003
-WATER Prototype
-Universidade Federal
de Uberlândia, Brazil
-Scientific
Development
- 2002
-School_Lab Reactor
-DLR, Cologne
- 2005
-SOWARLA concept
-DLR and Hirschmann Laborgeräte
-Industrial
Development

DLR Site Lampoldshausen
A Center for Space Propulsion Development & Tests



(Test of Ariane main propulsion with H_2/O_2)

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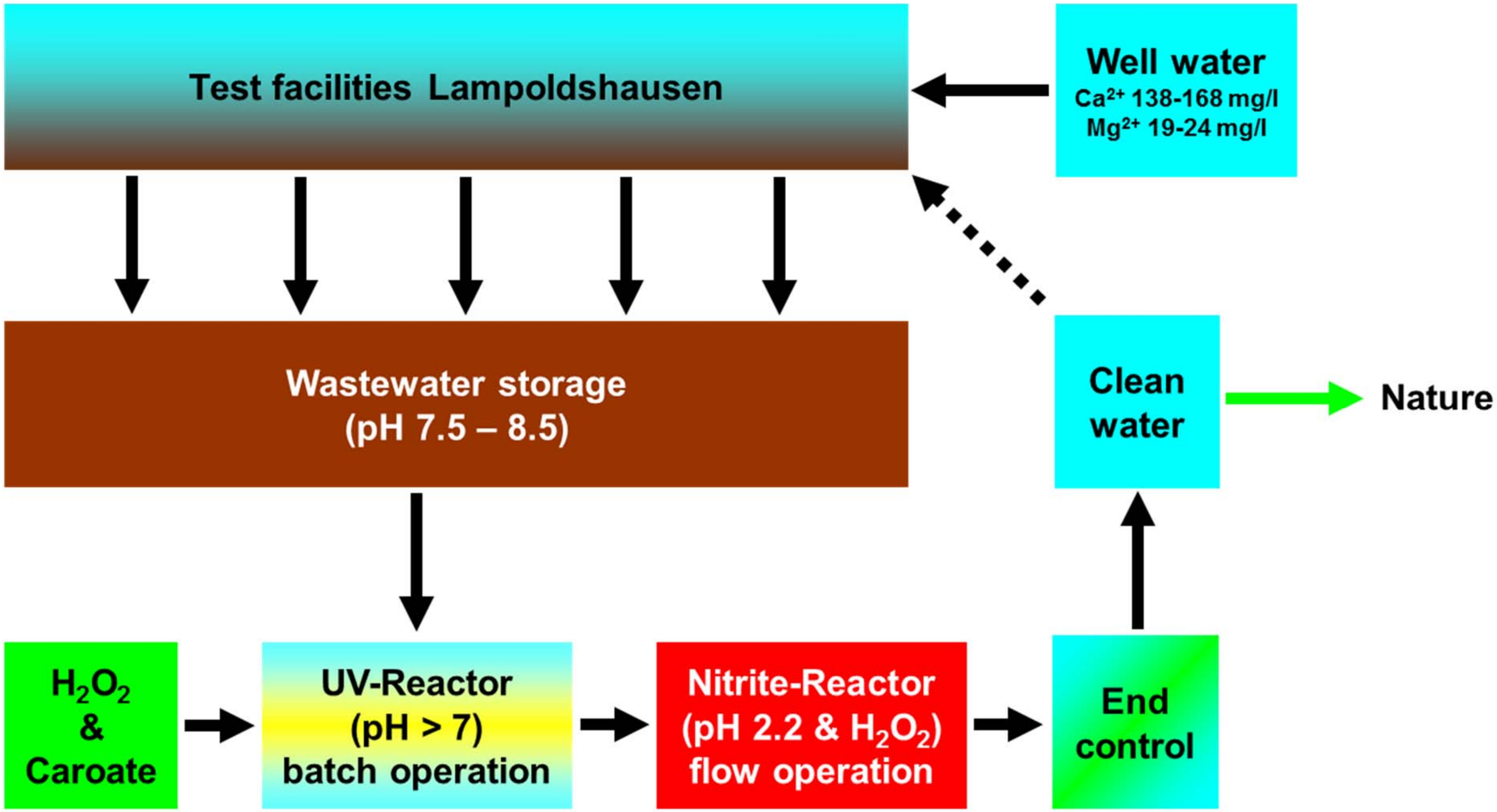
Space Propulsion Tests with Hypergolic Propellants

- Hypergolic fuels
    - $H_2N\text{-}NH_2$ (**HH**) + N_2O_4/NO
    - $(H_3C)NH\text{-}NH_2$ (**MMH**) + N_2O_4/NO
    - $(H_3C)_2N\text{-}NH_2$ (**UDMH**) + N_2O_4/NO

- Cooling water contaminations
    - **HH** / **MMH** / **UDMH**: ~0.5-2 mg/l
      (max. 50-80 mg/l from tank cleaning)
    - **Nitrite**: ~10 mg/l (max. 50-100 mg/l)

Water Treatment in Lampoldshausen

Combination of Photochemical & Chemical Methods



Water Treatment in Lampoldshausen
Combination of Photochemical & Chemical Methods

Annual mean values (2005-2007)	
Wastewater amount	4,694 m^3
Caroate	433 kg
Hydrogen peroxide (35%ig)	3,843 kg
Sulfuric acid (38%)	8,130 kg
Sodium hydroxide (33%)	8,474 kg
Medium pressure lamps	2
Activated Carbon (for COD)	1
Total energy demand	39 MWh

- Reliable detoxification below threshold limits
    - Hydrazine < 0.1 mg/l
    - Nitrite < 2 mg/l
- Considerable energy & chemicals demand
- Consumable costs ~4.60 €/m^3

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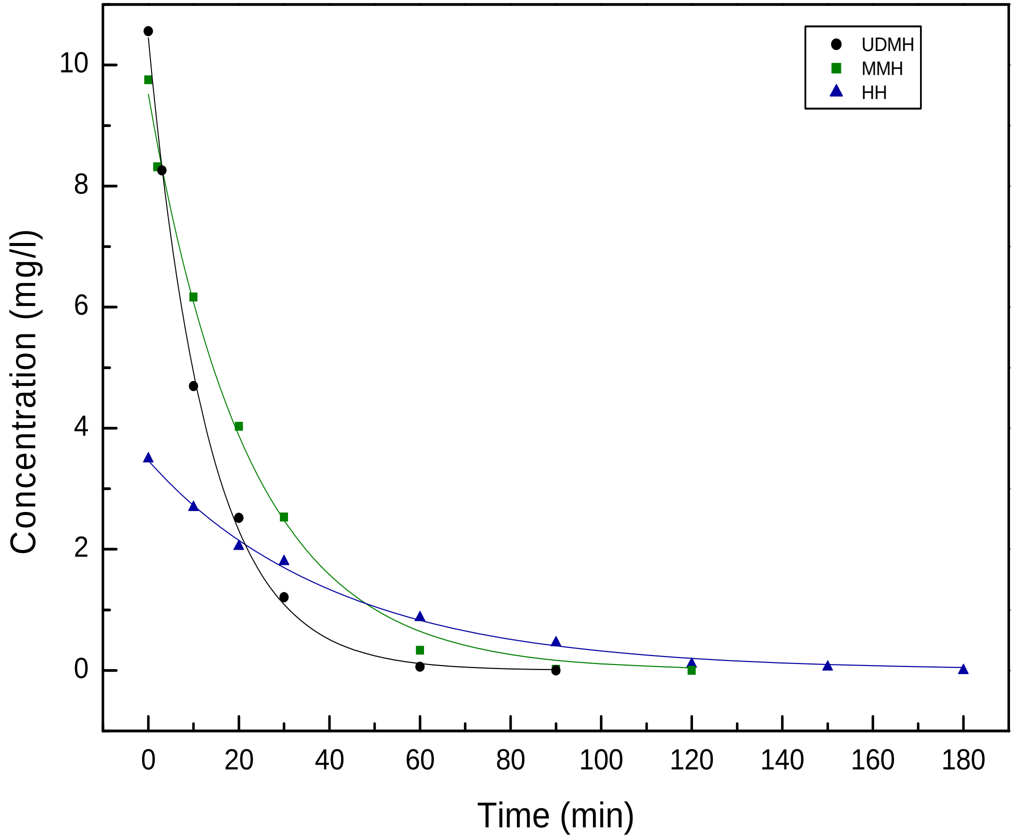
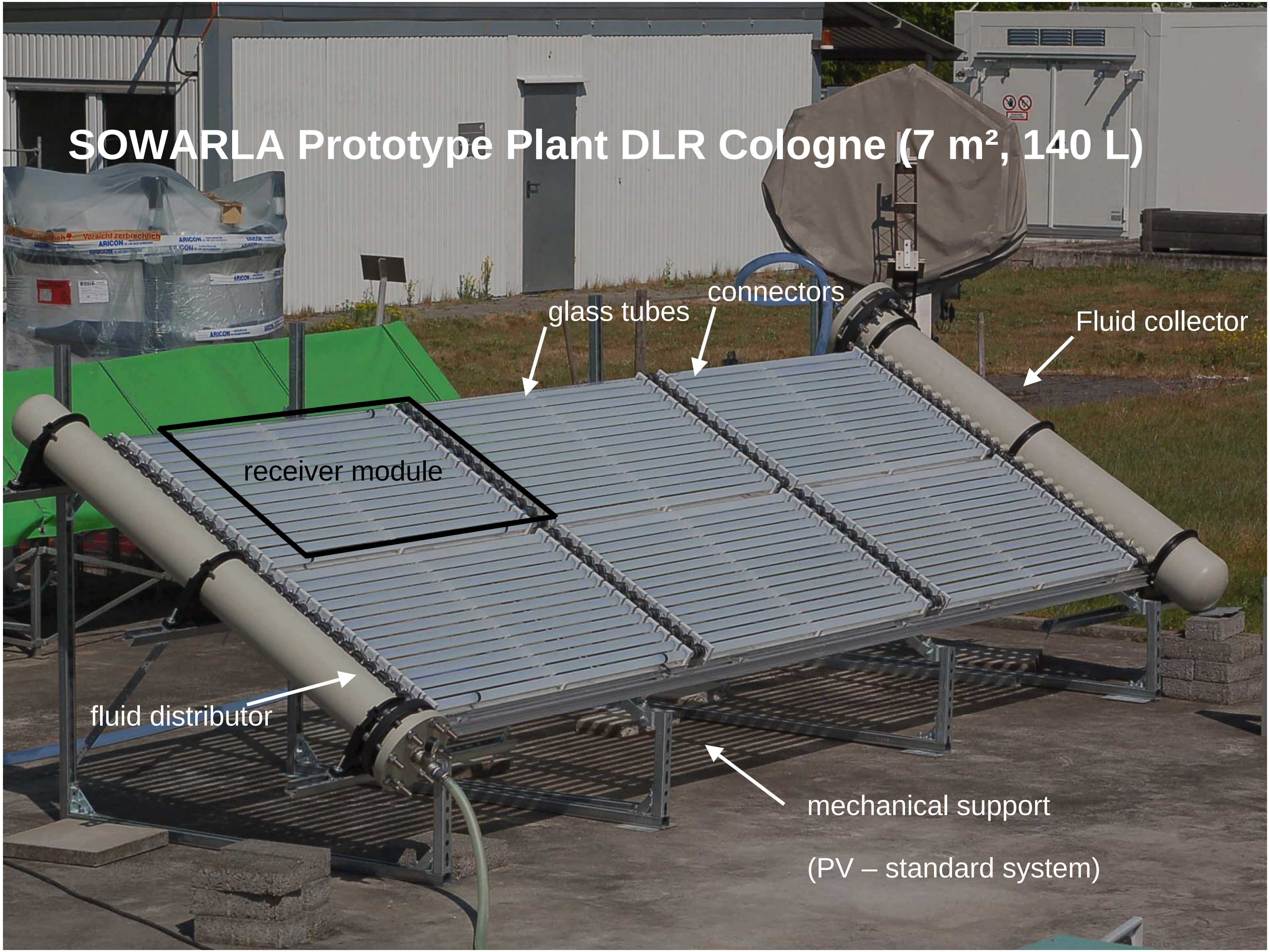
Degradation of Hydrazines via photo-Fenton and UVA



- Recirculating batch
- V_{batch} 4 - 5 L
- λ_{max} 365 nm
- P_{UV} 9.6 W

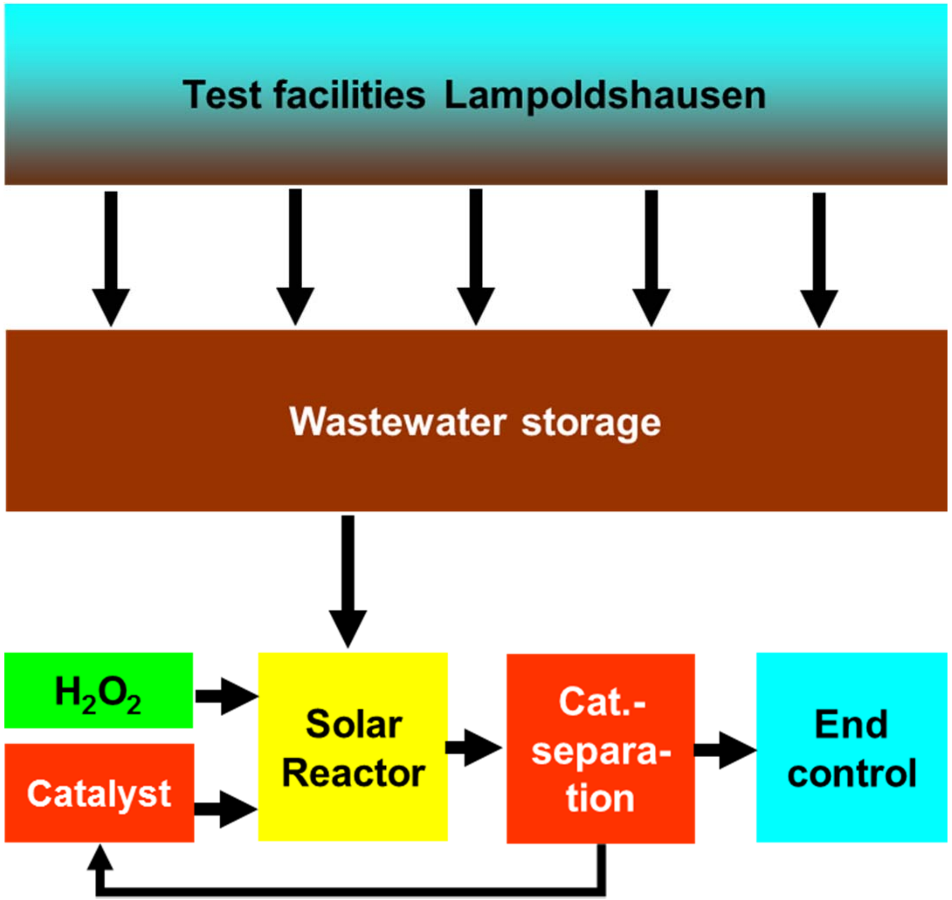
SOWARLA Prototype Plant DLR Cologne (7 m², 140 L)




SOWARLA Pilot Plant DLR Lampoldshausen
32 m² Receiver, 1,000 L, Roof Installation
fluid collector
glass tubes
receiver module
mechanical support
fluid distributor

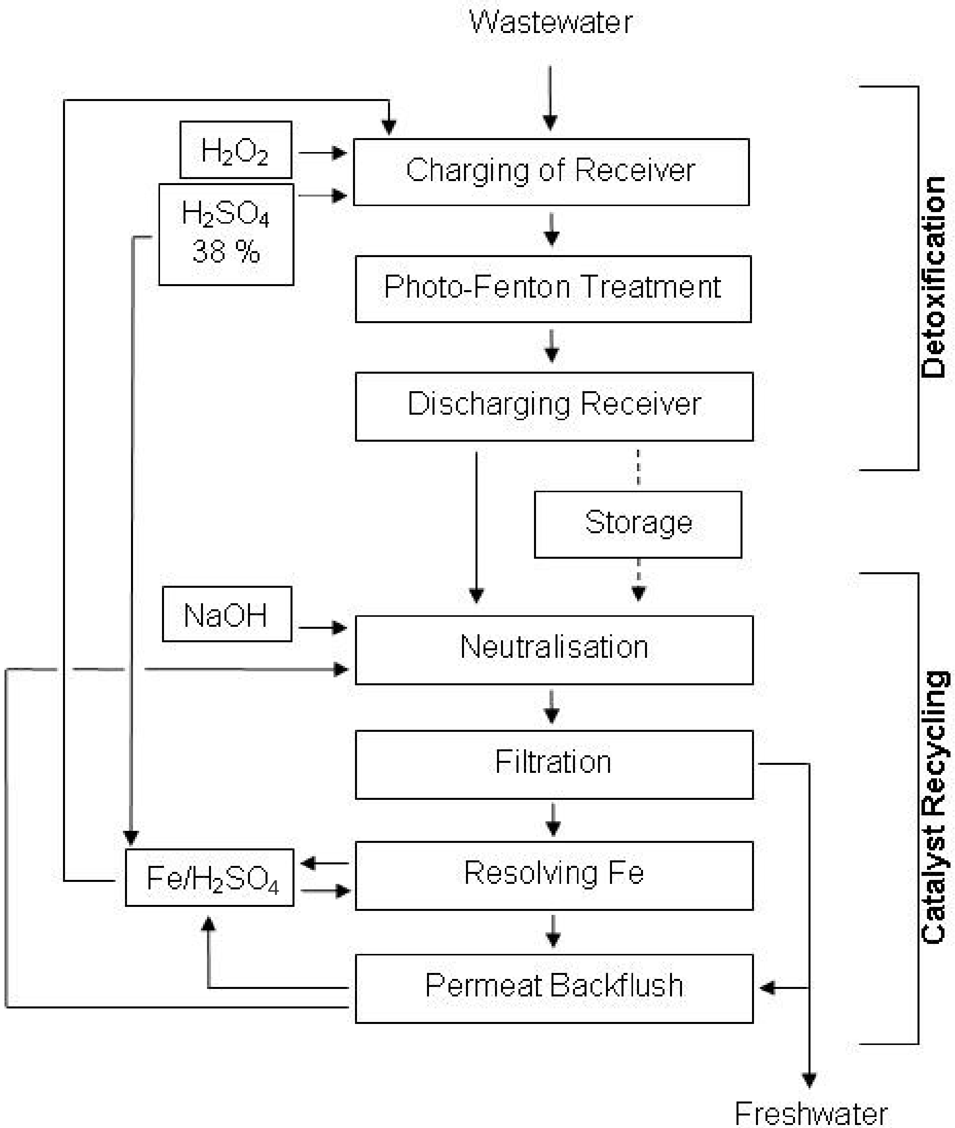

SOWARLA Demonstration Plant, Lampoldshausen
240 m² Receiver (4,500 L)
receiver module
water distribution and
collection
mechanical support

Integration of Solar Water Detoxification in LA

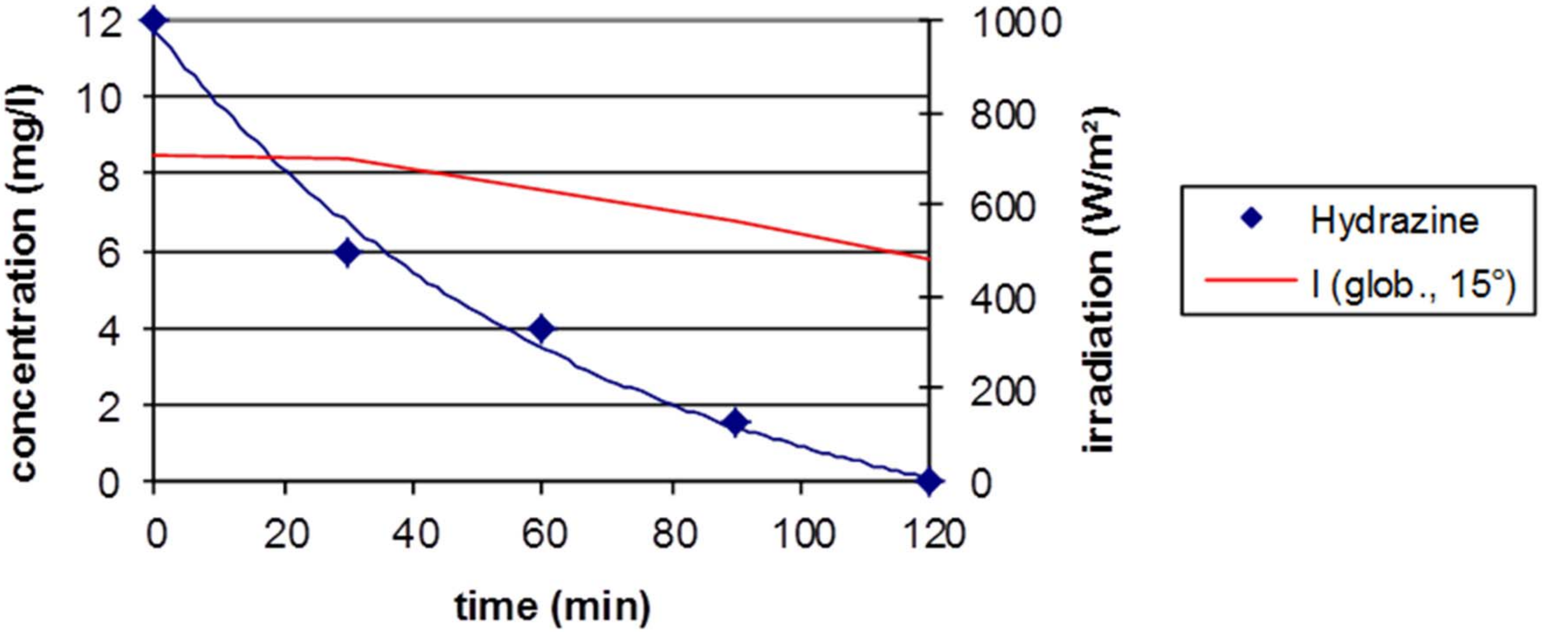


- Solar Fenton reaction as alternative to UV-reactor/nitrite-reactor
- UV-reactor/nitrite-reactor remain as back-up system
- Automatic (SPS) operation (filling, dosage, treatment, catalyst separation, discharge to end control)
- Operator maintains supply and provides concentration data (analysis of storage tanks and end control)

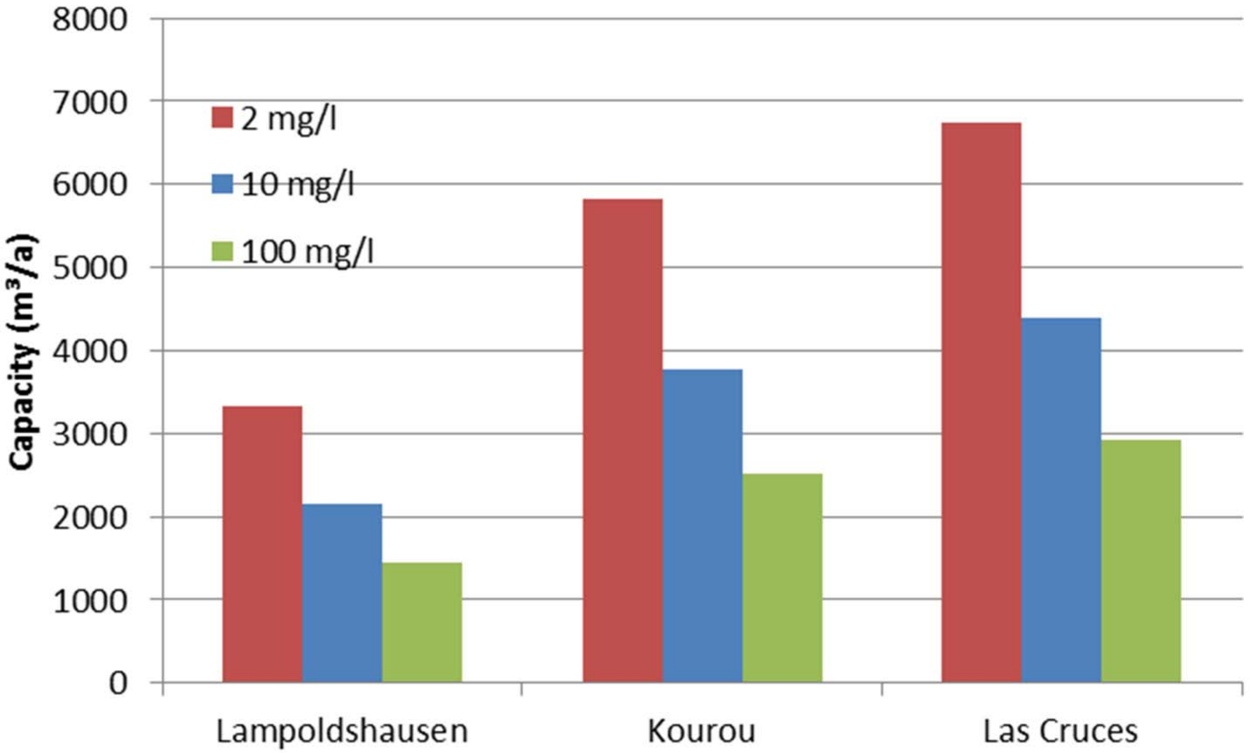
Process Design



Degradation of Hydrazine at Demo Scale



Annual Capacity for MMH Wastewater
Comparison of different plant locations



MMH to be degraded below 0.1 mg/l

Comparison of Consumable Costs for the LA case

	UV/NO_2^--reactor	Solar reactor
Oxidants (€)	3,667	754
Acid / base (€)	5,829	673
Lamps / activated carbon (€)	7,400	0
Electricity (€)	4,680	930
Sum (€)	21,575	2,357
Capacity (m³)	4,694	2,823
Costs (€/m³)	4.60	0.83

Transfer to other Applications

	MTBE (TOC, mg/L)	PCE mg/L	OECD sewage model (COD, mg/L)	Iopromide mg/L	Sulfamethoxazole mg/L	Caprolactam mg/L	(TOC, mg/L)
initial	68	10	800	5	1.5	115	73
end	17	0.1	400	0.3	0.01	0.1	4
Q_{glob} (Wh/l)	90 - 100	20 - 30	55 - 75	12	16	12	60
max. Capacity (m^3/a)							
LA	1,200 – 1,300	3,900 – 5,800	1,500 – 2,100	9,700	7,300	9,700	1,900
Kourou	2,000 – 2,300	6,800 – 10,200	2,700 – 3,700	17,000	12,800	17,000	3,400
Las Cruces	2,400 – 2,600	7,900 – 11,900	3,200 – 4,300	19,800	14,800	19,800	4,000

Energy dose (Q) from solar prototype or demonstration plant tests

Summary

- Scientific developments:
    - Explanation of the degradation mechanisms
    - Development of more efficient catalysts
    - Degradation of more contaminant classes

- Technological development
    - Receiver design
    - Scale-up
    - Demonstration

- Present state: the technology is ready for industrial use!

Project Partners and Support

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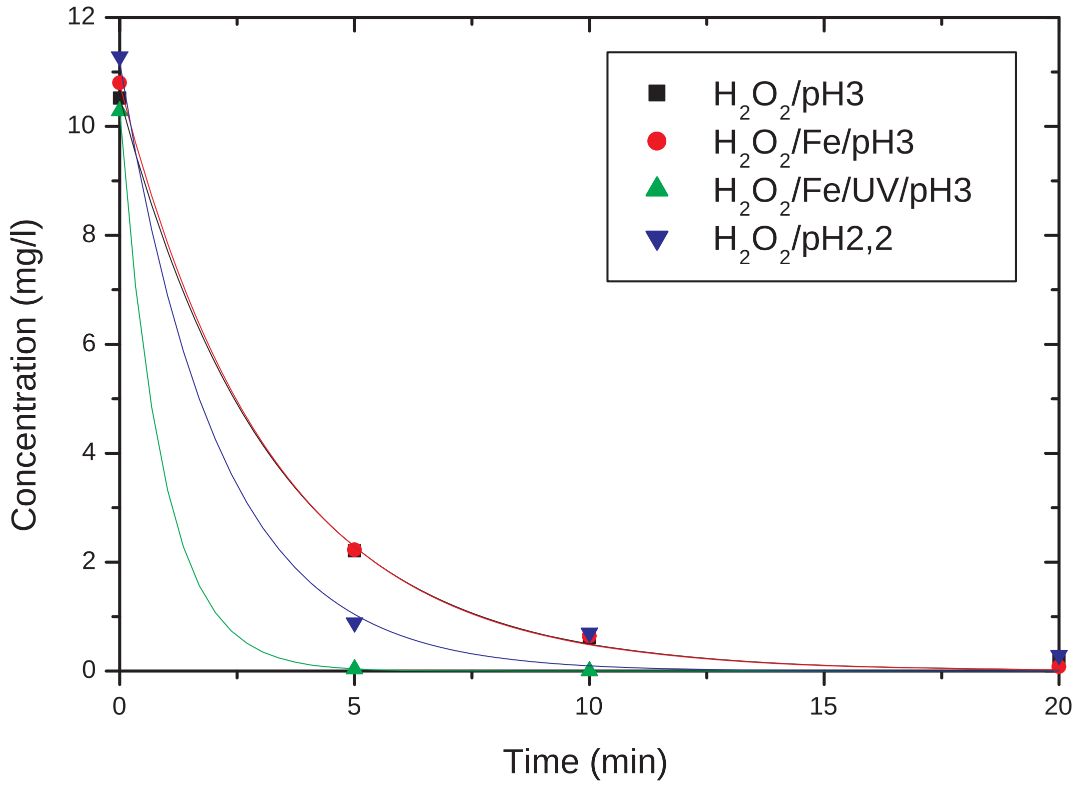
Nitrite in photo-Fenton Processes

- Fast Elimination enhanced by photo-Fenton conditions
- No formation of nitrite from nitrate with UVA
- Nitrite not important for batch time but for H_2O_2 dosage!



Degradation of UDMH at Demo Scale